Molecular systems for smart materials

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Chapter 3
Raman spectroscopy on modified electrodes

In this chapter the analysis of modified electrodes by Raman spectroscopy is presented, together with a brief introduction of the techniques employed. A key challenge in analysing compounds on surfaces is the low number of molecules available for investigation, especially in Self-Assembled Monolayers (SAMs). Two approaches to overcoming this limitation are discussed, resonance Raman spectroscopy to characterise phenomena observed by cyclic voltammetry (adsorption on an electrode) and surface enhanced Raman scattering (SERS) spectroscopy to characterise the binding of molecules to gold surfaces at submonolayer concentrations.

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Introduction

Considerable attention has been given recently to Self-Assembled Monolayers (SAMs) and molecularly modified surfaces.[1, 2] SAMs have proven important for applications in molecular electronics[3, 4], for bioassays[5, 6] and in material sciences for example as corrosion prevention layers[7] and as sensors.[8] One of the challenges in the use of SAMs is that the actual number of molecules present is too low to apply standard spectroscopic techniques for analysis. Indeed, only a limited number of techniques are available that provide structural information, including XPS, IR-, Raman, UV/Vis absorption and fluorescence spectroscopy. Many of these spectroscopy based techniques need specific adaptation to be able to measure the low amounts of compound on a surface. Electrochemistry is an especially well-developed method for the characterisation of SAMs.[9] However, this technique is easiest applicable if SAMs contain a redox active group. For redox active systems more information can be obtained by combining electrochemistry and spectroscopic methods *in situ*. In this chapter, two approaches using Raman spectroscopy are presented. The first example makes use of resonance enhancement of the intrinsically weak Raman signal to probe events occurring at an electrode. In the second example, SAMs are interrogated using roughened gold electrodes as substrate to take advantage of Surface Enhanced Raman Scattering (SERS) spectroscopy. Both methods for enhancement of the Raman signal will be discussed below.

Electrochemistry

In general, dynamic electrochemistry is used to study the changes in the oxidation state of a compound upon a change in applied potential, to determine the reduction-potential of a redox active compound.[9, 10] Standard solution electrochemistry employs either a two or three electrode arrangement. A working electrode and counter electrode are needed to carry current through a closed circuit. In a three electrode arrangement a reference electrode is employed, to accurately control the potential of the working electrode. Electrochemically unreactive electrolyte is added in excess, usually 0.1 M, both to increase the conductivity of the solution (to minimise ohmic potential drop over the solution) and to shield the analyte from the electric fields generated (to avoid electrophoretic effects and the generation of migration current). Analyte concentrations are typically in the millimolar range.

The most commonly applied electrochemical method is cyclic voltammetry. In this experiment the potential is cycled linearly and the current output is recorded. Upon oxidation or reduction of a compound in solution, an absolute increase in current output is observed. A typical cyclic voltammogram (CV) is shown in Figure 3-1.

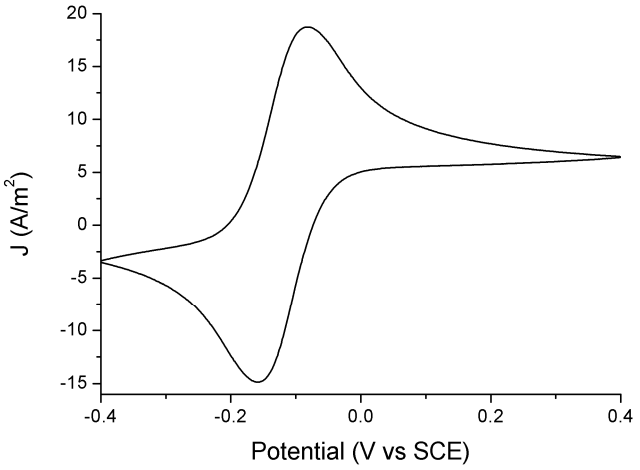

Figure 3-1 Cyclic voltammogram of decamethylferrocene in dichloromethane (0.1M $TBAPF_6$ (tetrabutylammonium hexafluorophosphate)), at a glassy carbon working electrode, Pt-wire counter electrode and SCE (Saturated Calomel Electrode) reference electrode.

In this cyclic voltammogram the redox couple Fe(II)/Fe(III) is observed at -0.1 V. Other electrochemical techniques used in this thesis are bulk electrolysis, sweep-step functions and dual electrode voltammetry for surface analysis.

Raman spectroscopy

Raman spectroscopy provides, in the first instance, vibrational information. The technique is complementary to IR spectroscopy, but based on a fundamentally different phenomenon and hence different selection rules are involved. The principle is shown schematically in Figure 3-2. Raman uses a monochromatic light source (e.g. a laser) as excitation source. When light interacts with a molecule scattering can occur, either elastically or inelastically. Excitation to a virtual state with instantaneous emission of the photon and no loss in energy normally occurs (Rayleigh scattering). Occasionally (in 1 out of 10^{12} times), a photon is scattered with loss or gain of energy.[11] The difference corresponds to the gap between vibrational levels of covalent bonds in the molecule. Promotion of a molecule to a higher vibrational level after excitation results in Stokes scattering. This scattered light has less energy than the excitation photon. If a molecule is already in a vibrational excited state it can be relaxed to the lowest vibrational level after excitation. This is called anti-Stokes scattering. The scattered light has more energy than the excitation light. This higher level is not populated significantly at room temperature, unless the energy gap equals k_BT, thus anti-Stokes scattering is generally much weaker than Stokes scattering.

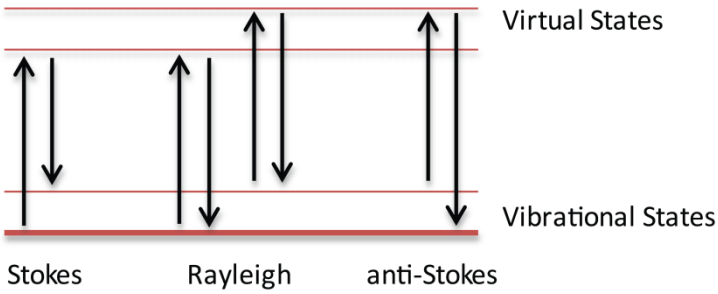

Figure 3-2 Elastic and inelastic scattering of incident light.[11]

Raman scattering is inherently weak. The intensity of the Raman signal obtained is dependent on the wavelength of excitation as well as on the polarisability of a compound and the detector/spectrometer efficiency. Methods to enhance the signal are available. First, by moving to shorter wavelengths (higher energy) of excitation, the probability of Raman scattering increases, with $I = 1 / \lambda^4$ dependence on wavelength. Secondly resonance enhancement can occur.[12] When the excitation wavelength is chosen to coincide with an electronic transition of the compound, enhancement of Raman scattering for specific modes associated with the electronic transition can occur. The signal can be enhanced by 10^3-10^6 in intensity.

A third method for increasing Raman scattering intensities is Surface Enhanced Raman Scattering (SERS). Rough gold surfaces and gold colloid are known to provide enhancement of Raman scattering of compounds in contact with the surface or between 'hotspots' on particles. The mechanism for this enhancement can be ascribed to two distinct phenomena; namely electromagnetic enhancement and chemical enhancement.[13] Part of the electromagnetic enhancement mechanism is resonance enhancement via the surface plasmon. As a gold surface is roughened, the plasmon shifts towards the red, allowing for SERS when excitation is in the same wavelength region. The second mechanism is ascribed to the effect of chemical interactions. Upon contact of a molecule with a surface, mixing of the molecular orbitals with the Fermi level of the gold can occur, resulting in partial charge transfer. A number of metals are available for obtaining SERS; most commonly gold and silver are used.[14]

Two general methods for obtaining SERS are readily applicable: gold or silver colloid can be used, or adsorption to a rough gold (macro) electrode can be performed, either by physisorption or chemisorption of the analyte.

An overview of the various methods of enhancement and their effects on the spectra obtained is given in Figure 3-3, using $[Ru(bpy)_3]^{2+}$. At λ_{exc} 785 nm enhancement of Raman scattering is not expected for a solid sample of the complex. In solution Raman spectra are not observed at low concentrations (< 10^{-3} M). However, at 10 µM resonance enhanced

spectra are easily obtained at λ_{exc} 449 nm, showing bands at the same position as the solid sample spectrum at λ_{exc} 785, but with a difference in the relative intensity of the bands. Resonance enhancement affects, in particular, vibrational modes that are coupled to that specific electronic transition, i.e. that undergo the greatest displacement in the transition. Finally both methods for obtaining SERS are demonstrated. The spectra obtained using gold colloid or on gold beads are similar, but broadening is observed for the latter case, due to different conformations on the surface, known to occur for low surface coverages.[15]

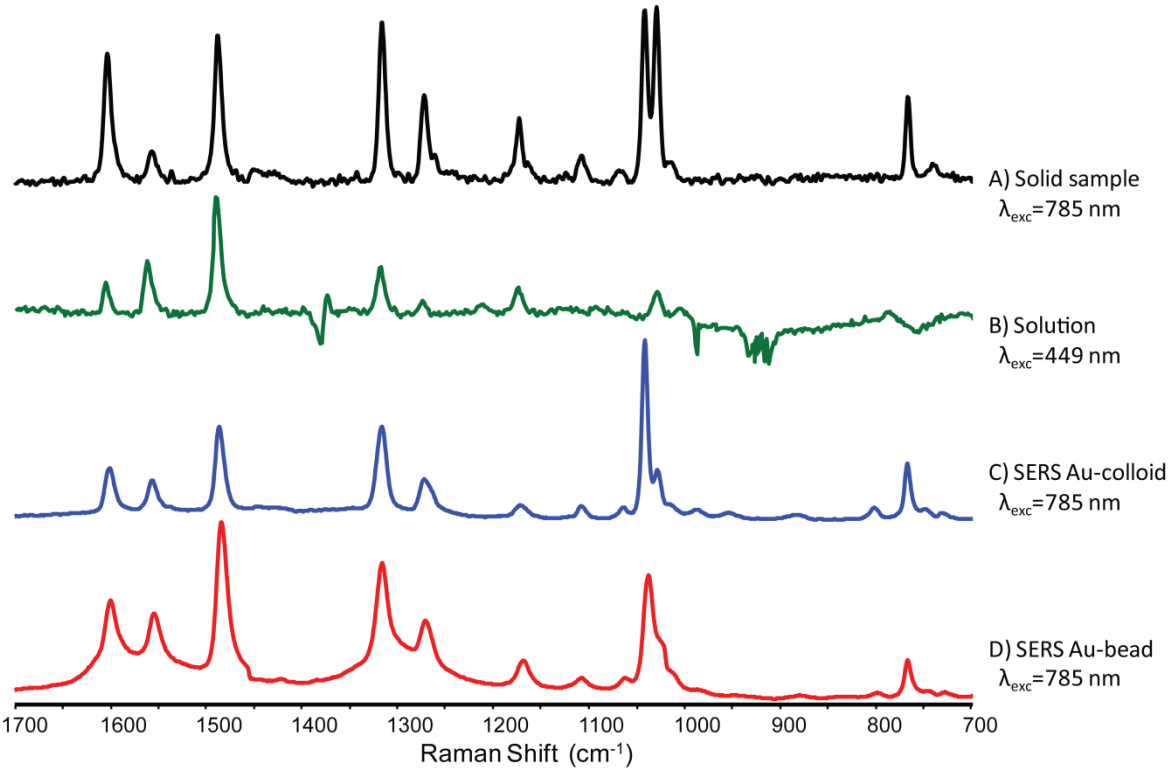

Figure 3-3 Raman spectrum of $[Ru(bpy)_3]^{2+}$ obtained with various methods. A) solid sample with λ_{exc} 785 nm (non-resonant Raman), B) Raman spectrum of solution of $[Ru(bpy)_3]^{2+}$ in CH_3CN at λ_{exc} 449 nm (RR), C) Raman spectrum in water using Au-colloid λ_{exc} 785 nm (SERS), D) Raman spectrum obtained upon physisorption on an electrochemically roughened gold bead λ_{exc} 785 nm (SERS).

In the following examples the versatility of resonance enhanced Raman spectroscopy is demonstrated. Both make use of enhanced Raman scattering to measure low concentrations of compounds at an electrode, but using two different methods to obtain the increase in intensity; i.e. Resonance Raman (RR) or Surface Enhanced Raman Scattering (SERS).

Results and discussion

Hexaphenylbenzene based switches

In this first example, Raman spectroscopy was applied to investigate the electrochemical behaviour of hexaphenylbenzene switches.[16] In the system studied, six dithienylethene

switches were attached to a central phenyl core (Figure 3-4). Two derivatives were prepared; one with a methoxyphenyl side group and one with a branched alkoxy as the side group. The synthesis of these hexaphenylbenzene switches was performed using a Co-catalyzed cyclotrimerisation.[16]

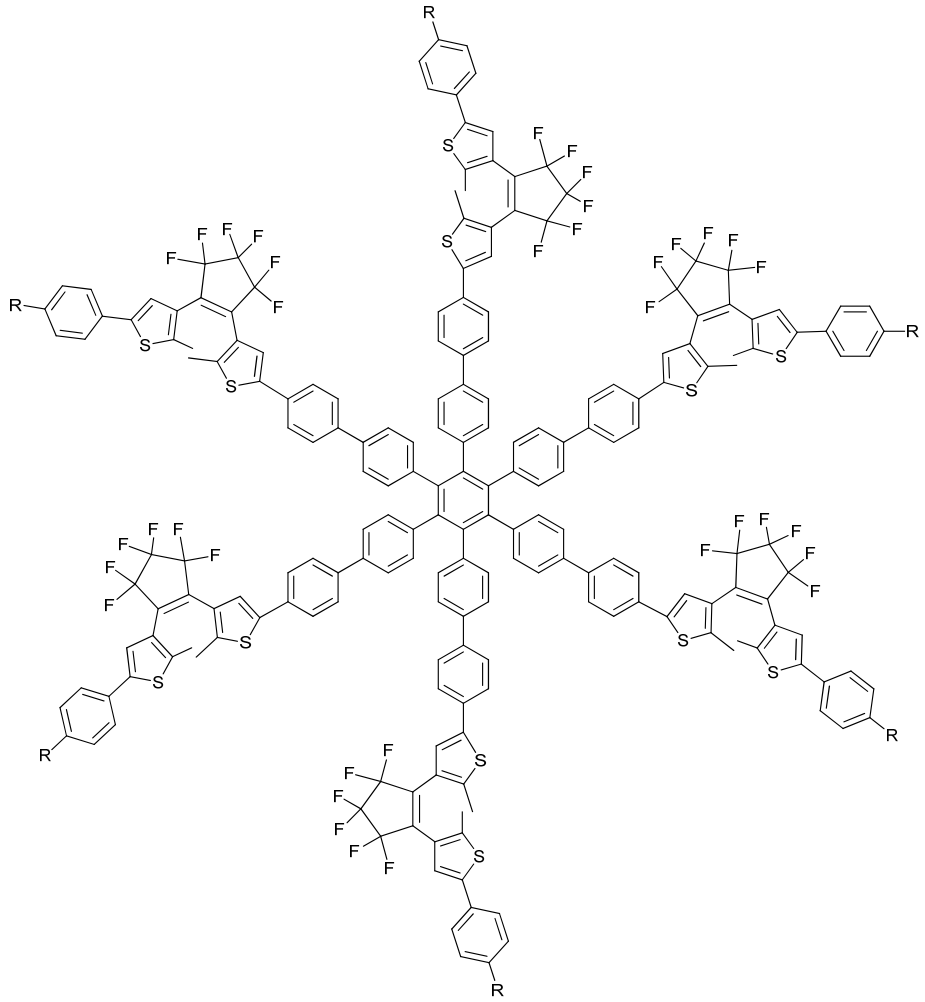

Figure 3-4 Hexaphenylbenzene switch studied in this chapter, **1** R = OMe, **2** R = $O(CH_2)_2CCH_3H(CH_2)_3CH(CH_3)_2$

The hexaphenylbenzene (HPB) dithienylethene switches **1** and **2** showed photochemistry corresponding to the common photoswitching expected for diarylethenes.[17, 18] The redox properties were studied by cyclic voltammetry, to determine if oxidative electrochemical switching could be achieved.[19, 20] Electrochemistry of the HPB switches showed an irreversible oxidation at 1.3 V (Figure 3-5), which corresponded to the oxidation of the open form to a dicationic species, after which ring closure occurred (see Chapter 1). All six switches underwent ring closing upon irradiation, and upon electrochemical oxidation.[16]

However, the cyclic voltammetry of the methoxyphenyl based HPB switch also showed a sharp spike prior to the reduction wave on the negative sweep from 1.6 V. This could be ascribed to desorption of deposited material from the electrode surface. Desorption spikes

are often observed when a change in solubility occurs upon oxidation or reduction.[9] It was postulated that the switch cation became insoluble upon oxidation and deposited in its cationic form on the electrode surface. In the present case, a multicationic species was formed, as each of the dithienylethene units in the molecule could be oxidised to a dication (i.e. an overall dodecacation). Raman spectroelectrochemistry was employed to investigate this. The wavelength chosen for the study was 785 nm, which coincides with the visible absorption of the monocation and dication at ca. 780 nm.

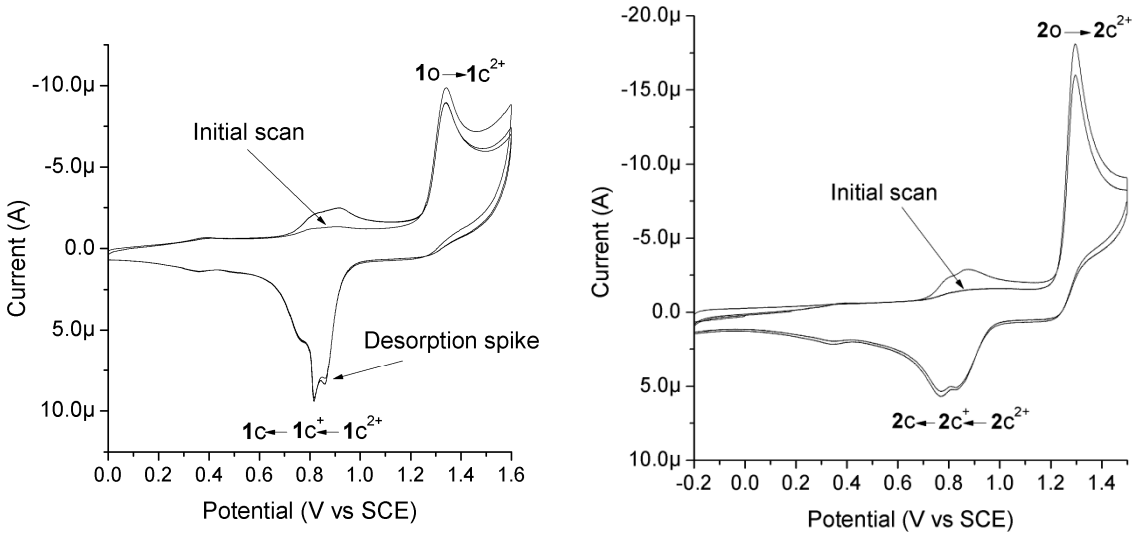

Figure 3-5 Cyclic Voltammetry of hexaphenylbenzene switches in 0.1 M $TBAPF_6/CH_2Cl_2$ vs SCE at 0.1 V s^{-1}, left, **1** right, **2**.

Spectroelectrochemistry can potentially confirm that the observed spike is in fact a desorption spike and not due to degradation or polymerisation. The key advantage of Raman spectroscopy is that the confocal volume is small. Normally the low concentration of compounds at the electrode means that they are not detected. As the monocation is formed it will not be observed as the steady state concentration is too low at the electrode, due to diffusion away from the electrode. However, if the sample is concentrated in its cationic form at the electrode by deposition its resonance Raman spectrum can be observed. The excitation wavelength was chosen to provide resonance enhancement for the charged species, but not for the neutral species.

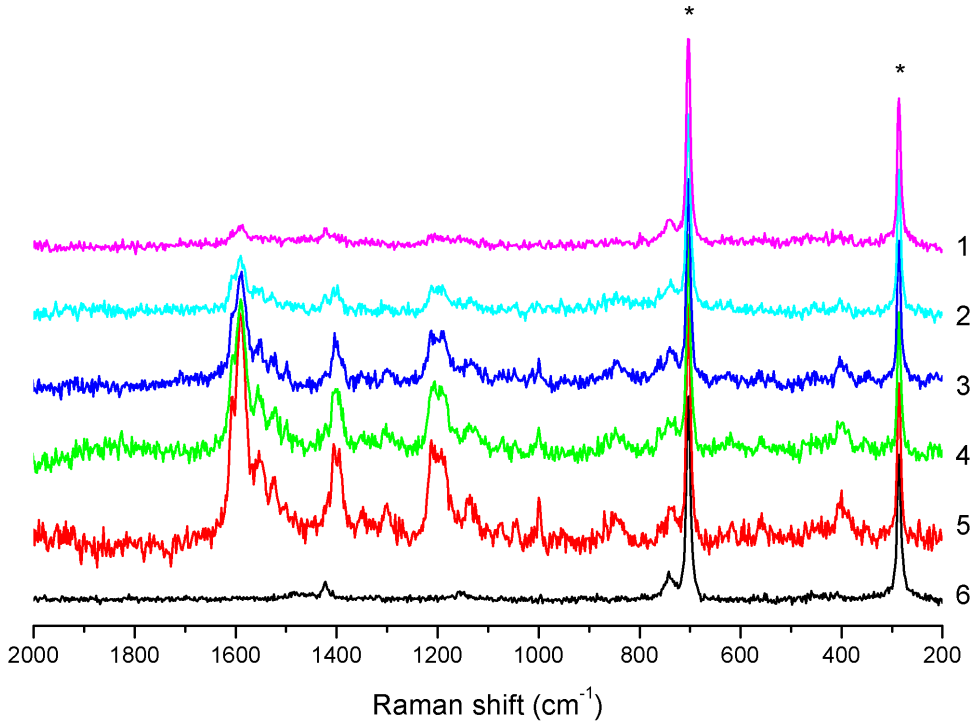

Figure 3-6 Raman spectra recorded during cyclic voltammetry of **1o**. Spectra 1-3, at 1.20 V, formation of a polycation occurs on the electrode;, spectra 4 and 5, cycling the potential back to 0.7 V, stable signal of polycation; and spectrum 6, below 0.7 V, neutral species. (CV From 0 to 1.25 V, at 0.05 V/s, 4 sweeps), Raman = kinetic series, 6 seconds between each spectrum acquisition, 2 seconds per acquisition, paused CV at 1.20 V to allow build-up of the polycation on the electrode. The asterisks denote solvent bands (0.1 M $TBAPF_6$ in CH_2Cl_2).

When the Raman probe was focused at the electrode, an increase in Raman scattering is observed over time upon oxidation at 1.2 V. The spectrum is assigned to the polycation of $\mathbf{1}^{n+}$. As the cyclic voltammetry is continued, the material remains at the electrode, until it is reduced at 0.7 V, where upon desorption occurs and the signal returns to zero. The increase in signal intensity can be ascribed partly to the resonance enhancement due to the absorption of the polycation at 785 nm. An increase in signal is also expected due to build-up of the material within the confocal volume of the Raman probe.

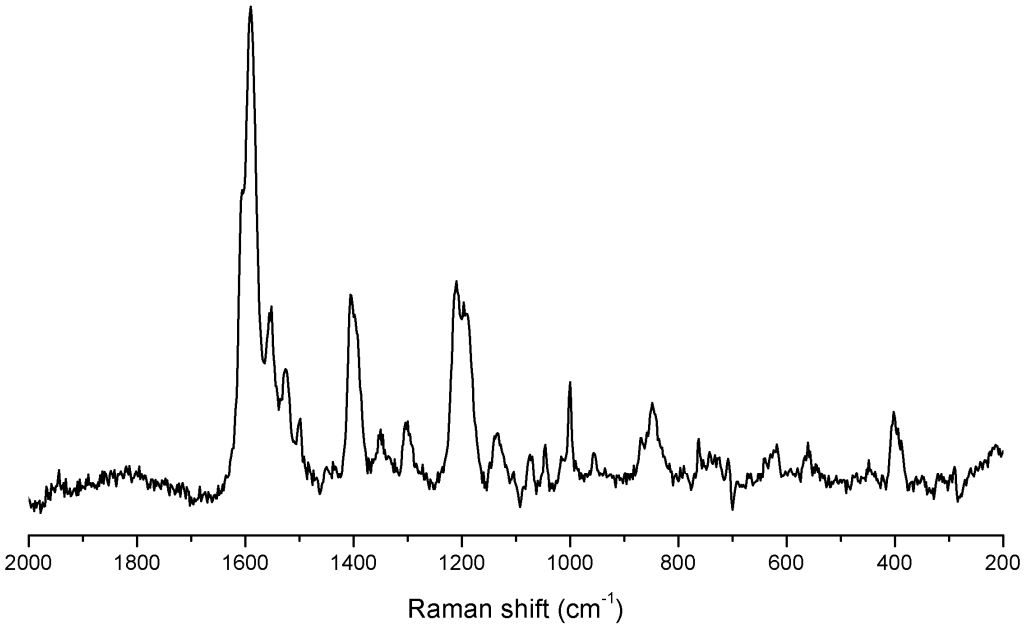

Figure 3-7 Raman spectrum of polycationic **1**, obtained by bulk electrolysis at 1.17 V.

To confirm that the Raman spectra obtained are due to the polycation of **1,** spectroelectrochemistry was also performed with **2**. A desorption spike was not observed in the cyclic voltammetry, which could be due to its increased solubility. The experimental arrangement used for **1** could therefore not be used to measure $\mathbf{2}^{n+}$ as the oxidised compound formed diffuses from the electrode before sufficient signal intensity is achieved. A different arrangement was employed using a thin layer cell with a glassy carbon disc working electrode held flush against the base of a quartz cuvette to limit diffusion. This held the polycation formed upon oxidation in proximity to the glassy carbon electrode and hence the confocal volume of the Raman probe (Figure 3-8).

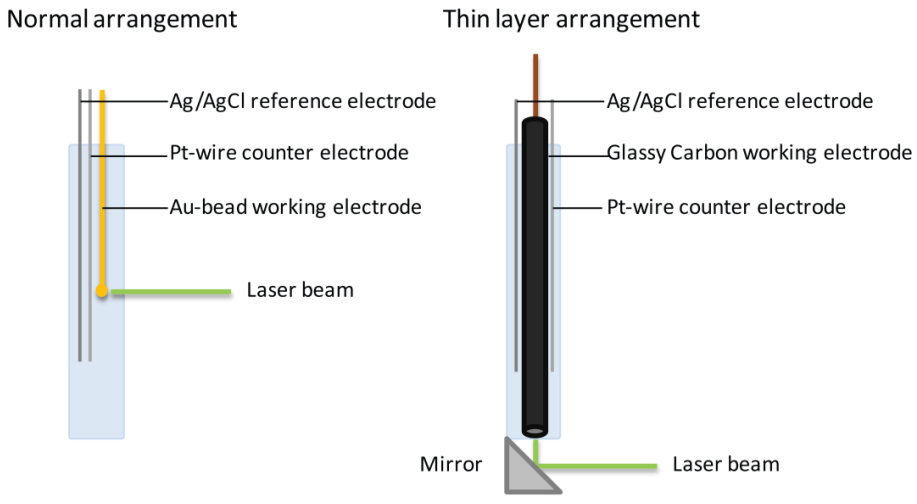

Figure 3-8 Arrangement for Raman spectroelectrochemistry using a gold bead working electrode, compared with thin layer Raman spectroelectrochemistry using a glassy carbon working electrode.

The spectra of **2** obtained upon oxidation are shown in Figure 3-9. The spectrum obtained at 0.0 V corresponds to a mixture of the open and closed forms of **2**. When a potential of 1.3 V was applied a spectrum similar to that of $\mathbf{1}^{n+}$ was observed. Importantly such a signal could not be obtained if diffusion was not restricted.

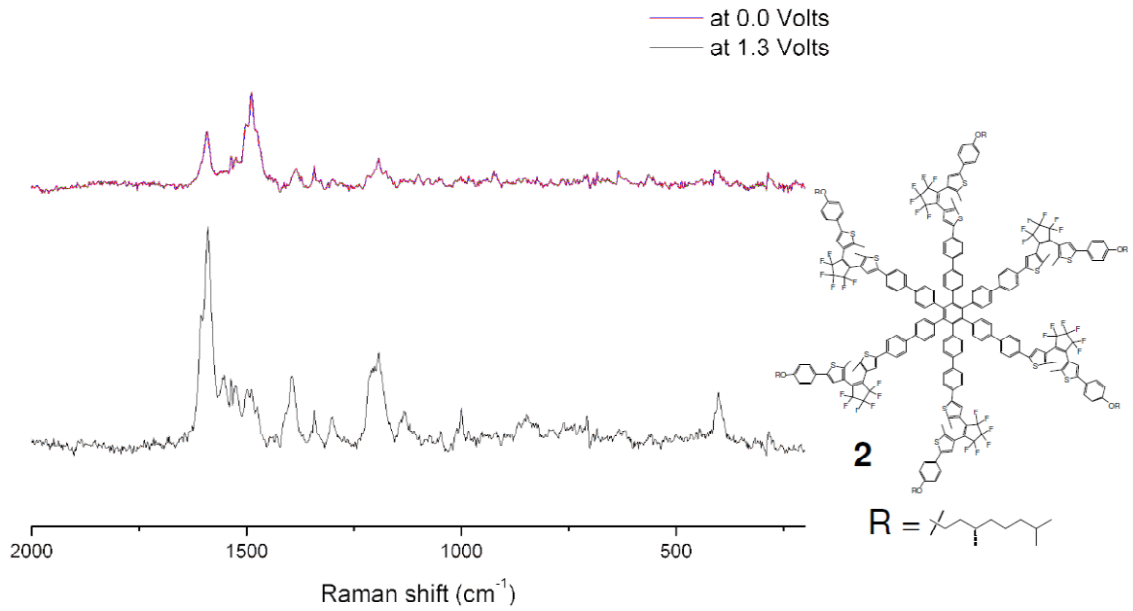

Figure 3-9 Spectroelectrochemical data for **2** (in 0.1 M $TBAPF_6$ in CH_2Cl_2) obtained using a thin layer cell. Raman spectrum at 0.0 V of the closed form (upper), spectra obtained upon oxidation to the polycation at 1.3 V (lower).

In this example the strength of resonance Raman spectroscopy and its application in a multi-technique approach are demonstrated. Low concentrations of adsorbed species could be measured by resonance enhancement of the Raman signal. The ability to focus on the electrode allowed for determination of processes occurring within small volumes (within the electrode diffuse layer).

Monolayers formed from Ruthenium complexes

Raman spectroscopy on electrodes was also applied in a second example. Monolayers of ruthenium complexes were formed on gold electrodes, using Ruthenium thiophene imidazolephenantroline bisbipyridine $[Ru(thimphen)(bpy)_2]^{2+}$ and Ruthenium pyridine imidazolephenantroline bisbipyridine $[Ru(pyrphen)(bpy)_2]^{2+}$ complexes.[21, 22] These complexes have potential use as components in molecular electronics.

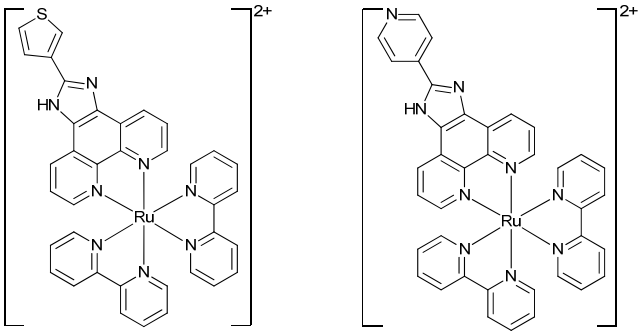

Figure 3-10 Ruthenium complexes used in monolayer formation, **3** $[Ru(thimphen)(bpy)_2]^{2+}$ and **4** $[Ru(pyrphen)(bpy)_2]^{2+}$.

The pyridine anchor group has previously been reported as suitable for preparing stable monolayers especially on Pt-electrodes.[23] However, thiophene as a surface anchor for monolayer formation has been explored much less.[24, 25] In this section SERS is employed to investigate the nature of the binding of thiophene to gold. A key question is in the nature of the bonding, i.e. chemisorption versus physisorption of these complexes to gold electrodes.

Monolayers of the Ruthenium polypyridyl complexes were prepared from solution as described by Cleary and Halpin.[21, 22] The electrochemical properties of the complexes in solution are reported elsewhere.[26] The surface coverage was found to be low (~ 10^{-11} mol/cm^2), which excludes the formation of multilayers. This is expected; as in earlier studies with charged Ru(II) and Os(II) complexes low surface coverage was also reported, due to electrostatic repulsion effects.[23]

Surface enhanced Raman spectroscopy was applied to obtain information about the structure of the complexes once immobilised on a gold electrode, and the relative importance of physisorption and chemisorption. Different approaches to obtaining SERS spectra are available and were compared in this study (Figure 3-11).

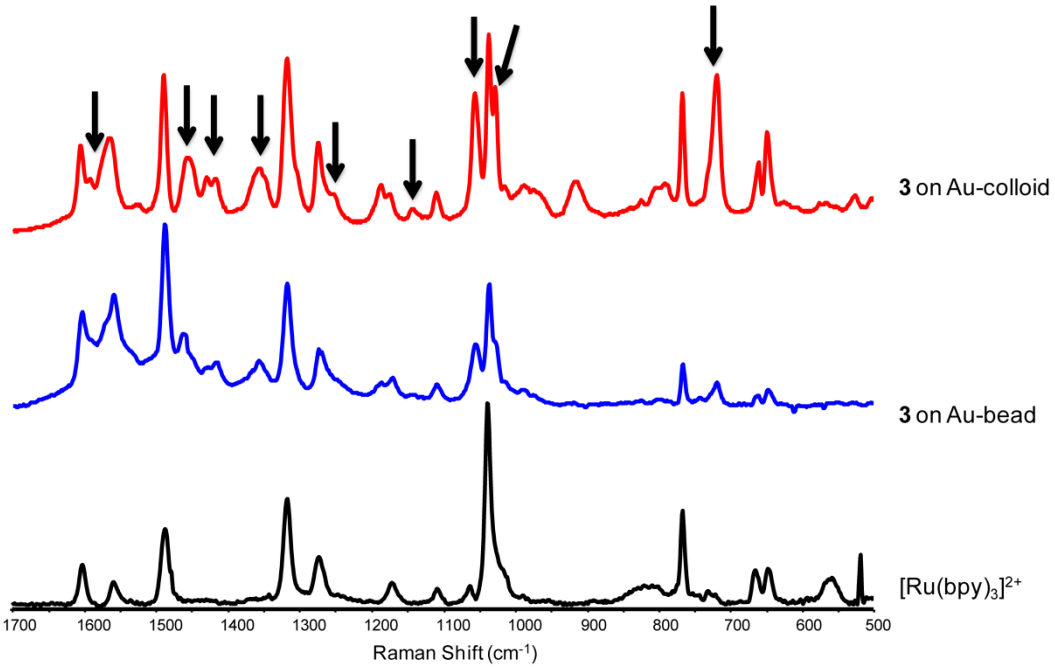

Figure 3-11 SERS spectra of $[Ru(thimphen)(bpy)_2]^{2+}$ (**3**) on Au colloid and on an electrochemically roughened Au bead. The SERS spectrum of $[Ru(bpy)_3]^{2+}$ is included for comparison. The arrows indicate bands from the thimphen ligand.

A difference in intensity for some bands as well as conformational broadening are observed when the spectra on a gold bead and on gold colloid are compared.[15] Especially in the low wavenumber region the intensity of the bands decreases upon monolayer formation. The binding of the thiophene to the gold may be responsible for this. The SERS spectra of **3** and **4** obtained using gold colloid were compared to assign the bands arising from thiophene vibrations (Figure 3-12).

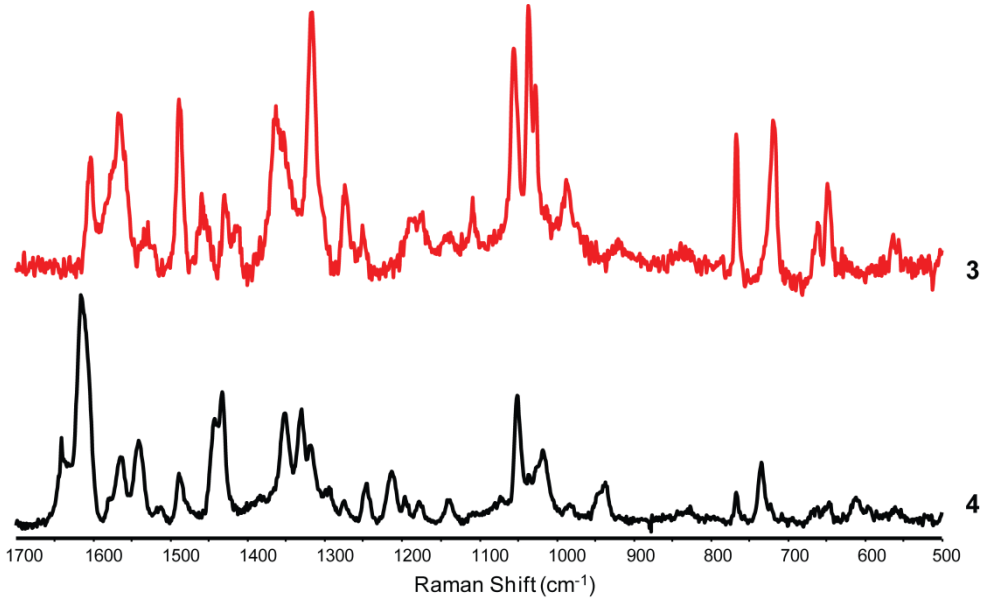

Figure 3-12 SERS spectra of complex **3** $[Ru(thimphen)(bpy)_2]^{2+}$ and **4** $[Ru(pyrphen)(bpy)_2]^{2+}$ obtained using gold colloid.

The bands at 720 and 1420 cm^{-1} are not observed in the spectrum of the $[Ru(pyrphen)(bpy)_2]^{2+}$ complex and may be assigned as thiophene bands. Raman spectra of monolayers on gold beads were followed over time. An increase and broadening of one band, at 650 cm^{-1} was observed over time, but with limited reproducibility. The band at 720 cm^{-1} decreased over time. The data indicates the thiophene group is affected upon adsorption to a surface, but it remains unclear what exact structural changes occur. Previous studies of SAMs of thiophene on gold using IR spectroscopy were performed by Shimoyama and co-workers.[24, 27] They also observed a change in intensity of the band at 720 cm^{-1} over time, which was assigned to a rearrangement in the packing of thiophene on the gold substrate. It was suggested that thiophene initially lays flat on the surface and over time rearranges to a tightly packed upstanding monolayer. However, the data presented in the papers did not support their conclusions. Besides, considering the geometry and measured surface densities of the complexes **3** and **4**, neither of these two modes of packing seems reasonable for these complexes.

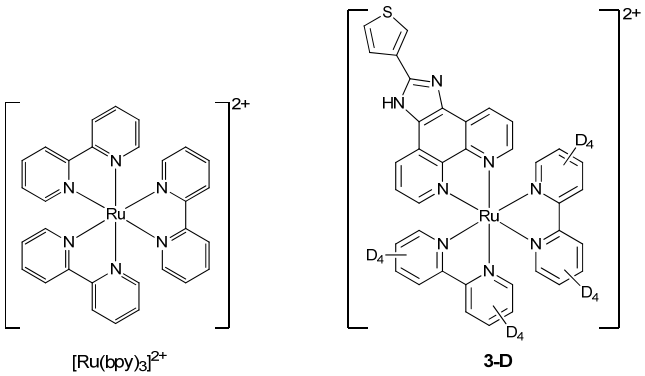

Figure 3-13 Structures of reference complexes used to assign the Raman bands, $[Ru(bpy)_3]^{2+}$ and **3-D** $[Ru(thimphen)(D_8\text{- }bpy)_2]^{2+}$.

Further assignment of the bands was made by comparison with the Raman spectra obtained for $[Ru(bpy)_3]^{2+}$ and a deuterated complex **3-D** (Figure 3-13). The bands arising from the bipyridine ligands are equal in Raman shift to the spectrum of $[Ru(bpy)_3]^{2+}$. Deuteration of only the bipyridine ligands in the complex confirms the assignment (Figure 3-14). The frequency of a vibration is sensitive to the reduced mass ($\mu = (m_1 * m_2) / (m_1 + m_2)$, where m_1 = atomic mass atom 1 and m_2 = atomic mass atom 2).[28] Upon changing to a heavier isotope, the band will shift to lower frequencies, hence lower wavenumbers.[I]

[I] However, Fermi resonance can occur when two bands are degenerate, which may complicate the actual shifts observed. If due to the deuteration one of those two bands changes in energy, a decoupling may occur, shifting one band to higher and the other band to lower wavenumbers.[32]

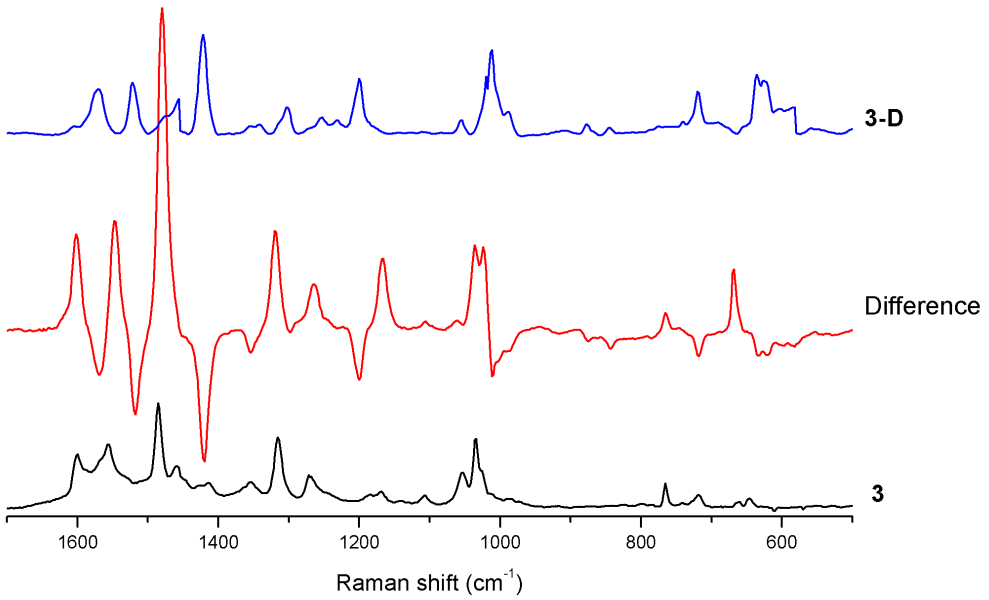

Figure 3-14 SERS spectra of deuterated complex $[Ru(thimphen)(D_8\text{-}bpy)_2]^{2+}$ compared with non-deuterated complex **3** (on an electrochemically roughened gold bead) (λ_{exc} 785 nm), in the middle is the difference spectrum, showing the bipyridine bands positive and the deuterated bipyridine bands negative.

An equimolar mixture of $[Ru(thimphen)(D_8\text{-}bpy)_2]^{2+}$ (**3-D**) and $[Ru(bpy)_3]^{2+}$ was used for SAM formation, to investigate the relative importance of chemisorption and physisorption. A SERS spectrum of the same solution was obtained from gold-colloid also; in this case the intensity ratio was different to the spectra obtained from SAMs on rough gold beads (Figure 3-15).

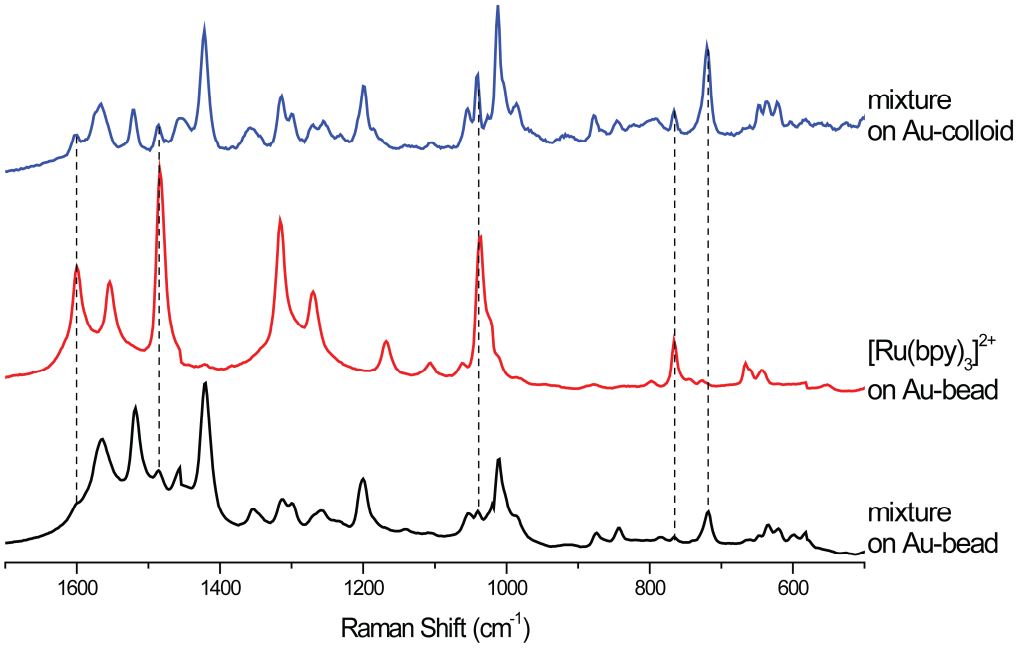

Figure 3-15 Competition experiment between **3-D** and $[Ru(bpy)_3]^{2+}$ in monolayer formation and physisorption; comparison with physisorbed $[Ru(bpy)_3]^{2+}$ (λ_{exc} 785 nm). An equimolar mixture of **3-D** and $[Ru(bpy)_3]^{2+}$ in ethanol was used in monolayer formation on a rough gold bead as well as being immediately studied using gold colloid. Bands from $[Ru(bpy)_3]^{2+}$ are indicated with dashed lines.

The competition experiment indicates a preference for binding of $[Ru(thimphen)(D_8\text{-}bpy)_2]^{2+}$ (**3-D**) over $[Ru(bpy)_3]^{2+}$ in monolayer formation. The intensity of the bands from **3-D** on the gold bead are much higher than the bands from $[Ru(bpy)_3]^{2+}$ compared to on the gold colloid (indicated with dashed lines in Figure 3-15). However, when the mixture was measured using SERS 'in solution' (using gold colloid) a much larger contribution from $[Ru(bpy)_3]^{2+}$ was observed. This demonstrated that the differences in intensity of the two complexes in the monolayer on a gold bead are not due to differences in resonance enhancement, but due to a different surface concentration of both complexes. Nevertheless, significant physisorption does take place, as evidenced by the observation of signals from $[Ru(bpy)_3]^{2+}$ on the gold bead electrode. However, binding via the thiophene is preferred, as a higher surface concentration of **3-D** with respect to $[Ru(bpy)_3]^{2+}$ is observed.
In this example the importance of correct assignment of Raman bands is demonstrated. Both comparison with a reference compound as well as isotope labelling allow for definitive assignment. Isotope labelling is also useful in analysing complex mixtures, as heavier atoms shifts the bands to lower wavenumbers in general, making it possible to analyse a mixture of two similar compounds.

Conclusions

In this chapter the application of resonance enhancement and SERS in tackling scientific questions with respect to molecular deposition on surfaces was demonstrated in two examples. The phenomenon observed in the electrochemistry of a hexaphenylbenzene dithienylethene switch (**1**) could be ascribed to desorption of the insoluble polycation, as it was reduced.
In the case of a new anchoring group for monolayers, submonolayer formation through chemisorption was confirmed by a competition experiment with $[Ru(bpy)_3]^{2+}$, which can only undergo physisorption. However, upon formation of monolayers, physisorption should nevertheless be considered, as signals from $[Ru(bpy)_3]^{2+}$ were observed on a gold bead electrode, also despite rigorous washing procedures being employed.

Acknowledgements

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Experimental section

Materials and instrumentation

$[Ru(bpy)_3](PF_6)_2$ was prepared according to literature procedures.[29] All chemicals were purchased from Aldrich, Acros, or Fluka. All solvents used were analytical grade or better unless stated otherwise. Electrochemical measurements were carried out using a CHInstruments 600C or 760C (bi) potentiostat. All potentials are quoted with respect to the Saturated Calomel Electrode (SCE).

Raman spectroscopy

A Perkin Elmer Raman station/microscope was used to record spectra at λ_{exc} 785 nm (300 mW DPSS laser, 80 mW at sample, Perkin Elmer). All laser sources were non-polarised at sample. For Raman spectroelectrochemistry a gold bead working electrode was employed (formed by melting gold wire using a hydrogen flame). The bead was cleaned electrochemically by oxidation in 0.5 M H_2SO_4 (aq) and subsequent stripping in 0.1 M HCl (aq) followed by cycling between -0.4 to 1.2 V vs. $Hg/HgSO_4$ in 0.5 M H_2SO_4 (aq) for 20 cycles. Raman spectra are solvent subtracted and baseline corrected unless noted otherwise.

Monolayer preparation

Two different methods to obtain surface enhancement were used. The first method uses the aggregation of Au-colloid, which is a solution based technique. Each compound was dissolved in water prior to aggregation with Au colloid. Using an adapted procedure[30] originally described by Tian et al.[31] the gold beads were roughened in preparation for overnight deposition in solution of both of the Ruthenium complexes. The procedure starts with electrochemical cleaning in 0.5 M H_2SO_4, by cycling between -0.4 – 1.2 Volts vs $Hg/HgSO_4$, with Pt-wire as counter electrode. Subsequently electrochemical stripping was done using sweep-step functions, using 0.1 M KCl(aq) solution as the electrolyte, Pt-wire as counter electrode and a SCE reference electrode. The potential was increased from -0.3 to 1.2 V (vs SCE) at 1 V/s. The gold electrode was held at 1.2 V for 30 sec. Then the potential was swept back to -0.3 V with 0.5 V/s and kept at -0.3 V for 1.2 sec This procedure was repeated 24 times after which the surface of the gold electrode appears rusty brown in colour. The beads were left overnight in a 1 mg/mL solution in ethanol. Prior to measurements, physisorbed molecules were rinsed off by dipping in three different beakers with fresh ethanol. The Raman spectra obtained using Au beads were recorded in air.

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